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Chitin based polyurethanes using hydroxyl terminated polybutadiene, Part II: Morphological studies

Khalid Mahmood Zia[a,*], Naureen Aziz Qureshi[b], Mohammad Mujahid[c], Kashif Mahmood[a], Mohammad Zuber[a]

[a] Institute of Chemistry, Government College University, Faisalabad 38030, Pakistan
[b] Department of Wilde Life and Fisheries, Government College University, Faisalabad 38030, Pakistan
[c] School of Chemical & Materials Engineering, National University of Science & Technology, H-12, Islamabad, Pakistan

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ABSTRACT

Chitin-hydroxyl terminated polybutadiene (HTPB) based polyurethane (PU) was prepared and structure of the pre-designed PU was confirmed using FT-IR spectrometer. The FT-IR analysis confirmed that the crosslinking density increased with increasing the chitin contents in the final PU. During the detailed FT-IR study, it was observed that tri-functional character of chitin is responsible for the formation of network structure. The scanning electron microscope (SEM) analysis also confirmed the cross-linked structure of the material. The amount of carbon, nitrogen and oxygen elements obtained from EDX–SEM microanalysis also supported the results. The resistance in solubility against the solvent also confirmed the crosslinking behavior of the prepared polyurethane.

1. Introduction

Chitin is the most widespread biopolymer in nature after cellulose. Chitin and its derivatives have great economic value because of their biological activities, and their industrial and biomedical applications. It can be extracted from three sources, namely crustaceans, insects and microorganisms [1]. Chitin is a linear polysaccharide composed of α-(1-4)-linked 2-acetamido-2-deoxy-D-glucose units which may be de-*N*-acetylated to some extent. The chitin molecules are known to be ordered into helicoidally micro-fibrillar structures that are embedded into the protein material of the shells. Chitin is closely associated with protein, minerals, lipids and pigments [2]. Polyurethane elastomers (PUEs) are possibly the most versatile classes of polymers due to their biocompatible behavior [3]. Molecular characterization, morphological studies and thermo-mechanical properties of PUEs using different diisocyanate and α,ω-alkane diols have been reported by many researchers [3–5]. Polyurethanes functionalized by polysaccharides have been presented in the literature time to time. Synthesis of polyurethanes using sugar [6], chalcone embedded polyurethanes as a biomaterial [7,8] and thermal-responsive chitin-based polyurethane copolymer as a smart material [9] have been comprehensively reviewed and documented. Surface morphology of starch [10], cellulose [11], and chitin–humic acid [12] has also been investigated and well documented. Starches modified with polyurethane microparticles [13], novel bio-antifelting agent based on waterborne polyurethane and cellulose nanocrystals [14], covalent incorporation of starch derivative into waterborne polyurethane [15] and role of starch nanocrystals and cellulose whiskers in synergistic reinforcement of waterborne polyurethane [16] have been reported in the literature. Regarding established literature on chitin based polyurethane synthesis, extensive work on structural characterization, crystalline patterns, and thermal properties of chitin-based polyurethane elastomers (PUEs) have been comprehensively reported elsewhere [17–19]. In vitro biocompatibility and cytotoxicity of chitin/1,4-butane diol blend based polyurethane elastomers have been reported in the literature [20,21]. Few reports have been found on the structural characterization of chitin-based polyurethane elastomers and their shape memory characteristics [22,23].

The professional literature and scientific writings have reported possible applications, preparation and properties of hydroxyl terminated polybutadiene based smart materials [24]. Considering excellent biocompatibility and wound healing properties of chitin, intelligent structural properties of hydroxyl terminated polybutadiene and good thermal, elastomeric and biocompatible behavior of polyurethane, the present project is designed to synthesize chitin based polyurethane using hydroxyl terminated polybutadiene.

* Corresponding author. Tel.: +92 300 6603967; fax: +92 041 9200671.
E-mail address: ziakmpkpolym@yahoo.com (K.M. Zia).

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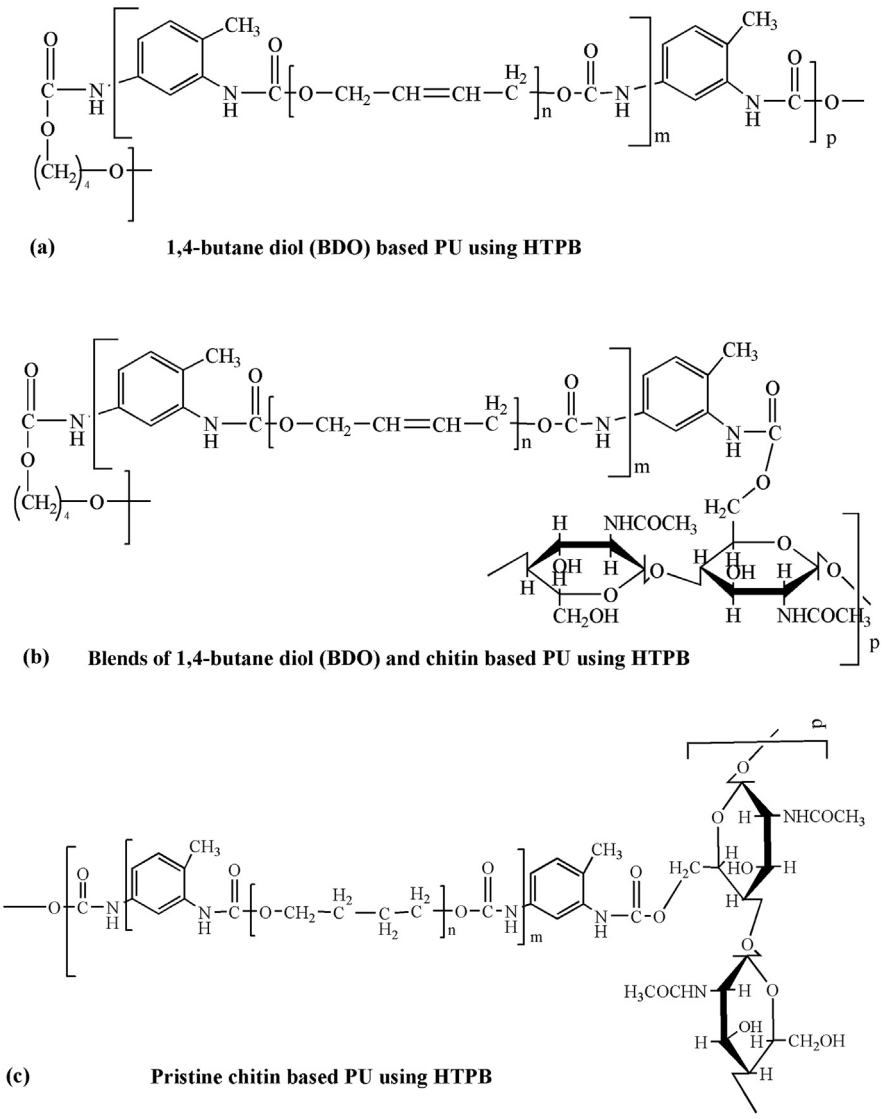

Fig. 1. Proposed structure of polyurethane using hydroxyl terminated polybutadiene as a polyol: (a) 1,4-butane diol (BDO) based polyurethane, (b) blends of 1,4-butane diol (BDO) and chitin based polyurethane, and (c) pristine chitin based polyurethane.

2. Experimental

2.1. Materials

2.1.1. Chemicals

Toluene diisocyanate (TDI), hydoxy terminated polybutadiene (HTPB), 1,4-butane diol (BDO) and chitin were purchased from Sigma Chemical Co. (Saint Louis, MO, USA). The HTPB and BDO used in this study were dried at 80 °C in vacuo for 24 h before use to ensure the removal of all air bubbles and water vapors that may otherwise interfere with the isocyanate reactions. The molecular weight of used polyol (HTPB) was confirmed by following the procedure reported in ASTM D-4274C [25]. TDI and all of the other materials were used as received. All of the reagents used in this study were of analytical grade.

2.2. Synthesis of polyurethane

The synthesis of PU prepolymer was carried out according to recommended procedure [17]. The detailed procedure for the synthesis of 1,4-butane diol based polyurethane, using blends of 1,4-butane/chitin based polyurethane and pristine chitin based polyurethane using hydroxyl terminated poly(butadiene) as soft segment are presented in our previous study [26]. The detailed formulations for the synthesis of different polyurethane samples by varying the chain extension material are given in Table 1. The proposed chemical structure of polyurethanes based on BDO, blends of BDO/chitin and pristine chitin are shown in Fig. 1.

2.3. Molecular characterization

Molecular structure of proposed synthesized BDO, BDO/chitin and pristine chitin based polyurethane using hydroxyl terminated polybutadiene was confirmed using Fourier Transform Infrared (FT-IR) spectroscopy. FT-IR scans of the prepared copolymer samples were obtained in the transmission mode using a Shimadzu Fourier Transform Infra-red (FT-IR) spectrometer.

2.4. Scanning electron microscopy

Small chitin based PU specimen was fit into the sample chamber, which could accommodate specimen up to 15 cm in height. PU specimen was made electrically conductive by coating with a thin